EUROPEAN PATENT SPECIFICATION

(54) Process for the extraction of metal values and novel metal extractants.

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Description

This invention relates to a process for the extraction of metal values from aqueous solutions of metal salts, and in particular to a process for the extraction of copper values from aqueous solutions in the presence of halide anions.

The use of solvent extraction techniques for the hydrometallurgical recovery of metal values from metal ores has been practised commercially for a number of years. For example copper may be recovered from oxide ores or from ore tailings by treating the crushed ore with sulphuric acid to give an aqueous solution of copper sulphate which is subsequently contacted with a solution in a water-immiscible organic solvent of a metal extractant whereby the copper values are selectively extracted into the organic solvent phase.

The general technique of copper recovery by solvent extraction is described in Encyclopedia of Chemical Technology (Kirk-Othmer) 3rd Edition, Volume 6 pages 850—851 published by John Wiley and sons.
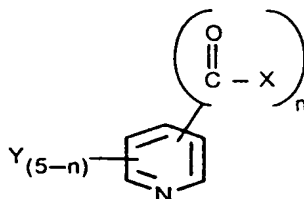
Our UK Patent No 1 421 766 describes the use of salicylaldoximes as extractants for this purpose.

In our US Patent No 4 039 612 we describe the use of certain heterocyclic compounds as extractants for use in removing metal values from solutions containing halide or pseudohalide ions. Such extractants include pyridines, imidazoles, thiazoles, benzimidazoles and quinolines. However, in general, the application of solvent extractant techniques to aqueous solutions containing halide ions has presented numerous technical problems.

Of particular importance in this connection is the development of hydrometallurgical routes (as an alternative to smelting) for the extraction of metal values from sulphur-containing ores such as chalcopyrite. Such ores may be leached for example using ferric chloride or cupric chloride solutions, but the solvent extraction of the resultant leach solution presents formidable difficulties.

The present invention provides a process for the extraction of copper values from aqueous solutions containing halide ions by the use of metal extractants whose several properties meet the stringent requirements imposed on the extractant by the system.

Accordingly, the present invention is a solvnt extraction process for extracting copper values from aqueous solutions of copper salts containing halide or pseudo halide anion which comprises the steps of (1) contacting the aqueous solution containing copper salts with a solution of an extractant in a water-immiscible organic solvent; (2) separating the aqueous solution from the solution of the extractant in the water-immiscible solvent into which copper has been extracted in the form of a complex of the copper and the extractant; and (3) contacting the resultant organic phase with an aqueous strip solution whereby the complex of copper with the extractant is unstable and copper transfers into the aqueous strip solution characterised in that the aqueous solution of copper salts containing halide or pseudo halide anion is contacted with a solution in a water-immiscible organic solvent of an extractant which is a substituted pyridine of formula:

wherein X is the group —OR$_1$ or —NR$_2$R$_3$, R$_1$ being a hydrocarbyl group containing from 5 to 36 carbon atoms and R$_2$ and R$_3$ being hydrogen or a hydrocarbyl group, R$_2$ and R$_3$ together containing from 5 to 36 carbon atoms, and n is 1, 2 or 3; and wherein Y is absent or is one or more, of the substituents halogen, alkyl, aryl, alkoxy, aryloxy, aralkyl, cyano, nitro or carboxylic acid.

When n is 2 or 3, the substituent —X in the respective groups —COX may be the same or different. For example, when n is 2, the two groups —COX may be —COR$_1$ and —COR$_1$' respectively where R$_1$ and R$_1$' are both hydrocarbyl groups containing from 5 to 36 carbon atoms. Similarly, when n is 2, the two groups —COX may be —COR$_1$ and —CONR$_2$R$_3$ respectively.

A further aspect of the invention provides a solvent extraction process for extracting copper values from aqueous solutions of copper salts containing halide or pseudo halide anion which comprises the steps (1) to (3) described above characterised in that the aqueous solution of copper salts containing halide or pseudo halide anion is contacted with a solution in a water-immiscible organic solvent of an extractant which is a substituted pyridine of formula:
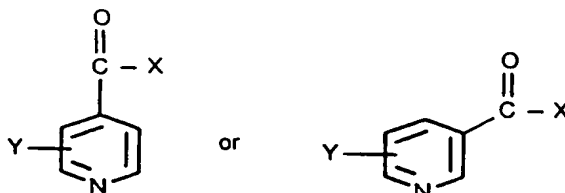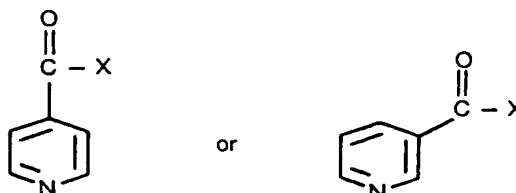
$$\underset{Y}{\overset{\overset{\textstyle O}{\underset{\|}{C}}-X}{\underset{N}{\bigcirc}}} \qquad \text{or} \qquad \underset{Y}{\overset{\overset{\textstyle O}{\underset{\|}{C}}-X}{\underset{N}{\bigcirc}}}$$

wherein X is the group —OR$_1$ or —NR$_2$R$_3$, R$_1$ being a hydrocarbyl group containing from 5 to 36 carbon atoms and R$_2$ and R$_3$ being hydrogen or a hydrocarbyl group, R$_2$ nd R$_3$ together containing from 5 to 20 carbon atoms, and wherein Y is absent or is one or more of the substituents halogen, alkyl, aryl, alkoxy, aryloxy, aralkyl, cyano, nitro or carboxylic acid.

According to a further aspect of the present invention there is provided novel metal extractants which are useful as extractants in the process described above. Thus there is provided a 3- or 4-substituted pyridine of the formula

$$\underset{N}{\overset{\overset{\textstyle O}{\underset{\|}{C}}-X}{\bigcirc}} \qquad \text{or} \qquad \underset{N}{\overset{\overset{\textstyle O}{\underset{\|}{C}}-X}{\bigcirc}}$$

wherein X is the group —OR$_1$ or —NR$_2$R$_3$, R$_1$ being an alkyl group containing from 9 to 24 carbon atoms and having the formula
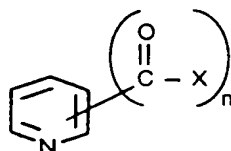
$$-CH_2-CH\underset{R_5}{\overset{R_4}{<}}$$
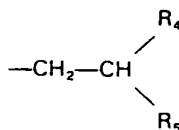
wherein R$_4$ and R$_5$ are alkyl groups, and R$_4$ contains two fewer carbon atoms than R$_5$, and R$_2$ and R$_3$ together containing a total of from 15 to 36 carbon atoms, provided that when R$_2$ is hydrogen, R$_3$ is a branched chain alkyl group.

There is also provided a substituted pyridine of formula:

$$\underset{N}{\bigcirc}\left(\overset{\overset{\textstyle O}{\underset{\|}{C}}-X}{}\right)_n$$

wherein X is the group —OR$_1$ or —NR$_2$R$_3$, and n is 2 or 3, the respective groups R$_1$ being alkyl groups containing a total of from 16 to 36 carbon atoms, and the respective groups R$_2$ and R$_3$ being alkyl groups wherein the total number of alkyl carbon atoms contained in all the respective groups R$_2$ and R$_3$ is from 20 to 70.

The pyridine ring may carry substituents in addition to the group(s) —COX. Examples of suitable substituents are halogen groups, alkyl groups, aryl groups, alkoxy groups, aryloxy groups, aralkyl groups, cyano groups and nitro groups. The pyridine ring may also carry a carboxylic acid group, and the invention includes for example a half ester of a pyridine dicarboxylic acid.

Substitution in the pyridine ring may for example result from the method of synthesis. For example bis ester of 4-phenylpyridine-3,5-dicarboxylic acid may be prepared from methyl propiolate, aromatic aldehydes and ammonium acetate in acetic acid followed by oxidation to the pyridine derivative and ester exchange (Chennat and Eisner, J.C.S. Perkin I, 1975).

When n is 1, examples of compounds which may be used in the process of the invention include esters or amides of nicotinic acids, isonicotinic acids and picolinic acids. When n is 2, examples of compounds which may be used in the process of the present invention include bis esters or amides of pyridine-2,4-dicarboxylic acid, of pyridine-2,5-dicarboxylic acid, and of pyridine-3,5-dicarboxylic acid. When n is 3, examples, of compounds which may be used in the process of the present invention include tris esters or amides of pyridine-2,4,6-tricarboxylic acid. Mixtures of such compounds may be used, for example a mixture of bis esters or amides of isomeric pyridine-dicarboxylic acids.

The substituted pyridines of the present invention wherein X is the group —OR$_1$ may be prepared by

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conventional means, for example by the reaction of a pyridine carboxylic acid, for example isonicotinic acids, nicotinic acids or picolinic acids respectively with the appropriate alcohol to form the desired esters. Alternatively the lower esters, for example methyl or ethyl esters may be subjected to ester exchange reactions with higher alcohols, or the acid chlorides may be reacted with the appropriate alcohol or phenol. Dicarboxylic acid esters of pyridine may conveniently be prepared from lutidines, for example by oxidation and esterification.

R_1 may for example be an alkyl grouup, for example an octyl, nonyl, decyl, dodecyl, tridecyl, pentadecyl, hexadecyl or octadecyl group or substituted alkyl group, for example a group containing one or more propylene oxide residues formed by reacting propylene oxide with an alcohol before esterification to give the substituted pyridine; R_1 may be a cyclo alkyl group such as cyclohexyl; R_1 may be an aralkyl group such as benzyl; or R_1 may be an aryl, alkylaryl or alkoxyaryl group for example p-nonylphenyl or p-dodecylphenyl.
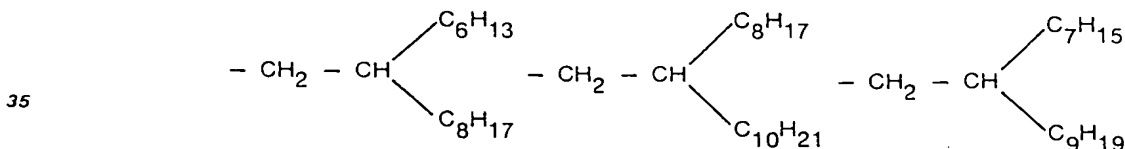
When n is 1 and there are no other substituents in the pyridine ring, R_1 is preferably a branched chain alkyl group containing from 9 to 24 carbon atoms.

R_1 may be an isomeric mixture of groups containing the same number of carbon atoms or a mixture of groups containing different numbers of carbon atoms (which may themselves be an isomeric mixture), for example a mixture of different alkyl groups. If R_1 is a mixture of groups containing different numbers of carbon atoms, the average number of carbon atoms is preferably from 9 to 24.

Highly branched groups R_1 may usefully be obtained by the reaction of the pyridine carboxylic acid with alcohols prepared by the Guerbet and Aldol condensations. Such alcohols are characterised by branching at the position beta to the hydroxyl group, and have the general formula:
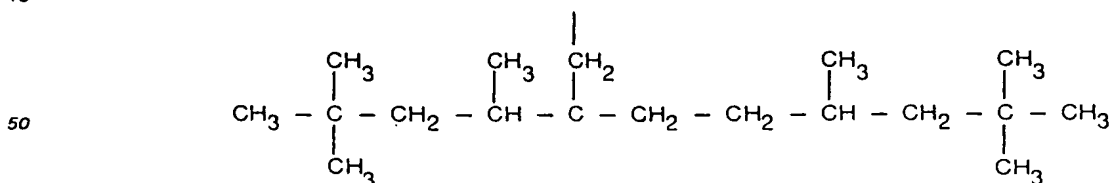
$$HO-CH_2-CH \big< {}^{R_4}_{R_5}$$

In general R_4 contains 2 fewer carbon atoms than R_5, and groups R_1 derived from these alcohols include for example,

$$-CH_2-CH\big<{}^{C_6H_{13}}_{C_8H_{17}} \qquad -CH_2-CH\big<{}^{C_8H_{17}}_{C_{10}H_{21}} \qquad -CH_2-CH\big<{}^{C_7H_{15}}_{C_9H_{19}}$$

R_4 and R_5 may be straight chain or branched chain alkyl groups and may be isomeric mixtures of alkyl groups. A mixture of highly branched alcohols may be obtained by Guerbet or Aldol condensations of mixtures of alcohols and aldehydes respectively.

Excellent solubility is conferred upon the compounds of formula I where the alcohol is the product of the aldol dimerisation of commercial nonaldehyde. In this alcohol the group R_1 is believed to consist essentially of a mixture of geometrical isomers of a radical of the formula:

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{}{\overset{\overset{CH_3}{|}}{CH}}-\underset{\underset{}{|}}{\overset{\overset{CH_2}{|}}{C}}-CH_2-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

When n is 2, the respective groups R_1 (R_1 and R_1') may be any of those groups R_1 listed previously. R_1 and R_1' are conveniently the same and are preferably straight chain or branched chain alkyl groups. When n is 2, we have found that to achieve the desired solubility of the metal complex in preferred solvents, R_1 and R_1' preferably together contain a total of from 16 to 36 carbon atoms. The groups R_1 may contain a mixture of isomers, for example a mixture of nonyl isomers derived from isononanol obtained by the hydroformylation of a mixture of octenes, a mixture of decyl isomers obtained from isodecanol, or a mixture of tridecyl isomers obtained from tridecanol.

The substituted pyridines of the present invention wherein X is the group $-NR_2R_3$ may be prepared by conventional means, for example by reaction of pyridine carboxylic acids and their lower esters with higher primary or secondary amines. Alternatively the acid chloride of the pyridine carboxylic acid may be reacted with the appropriate amine.

The amide group $-NR_2R_3$ may be primary (R_2 is hydrogen) or secondary. R_2 and R_3, which may be the

same or different may be groups of the type indicated above for R_1. R_2 and R_3 taken together contain from 5 to 36 carbon atoms. Thus R_2 may be for example a lower alkyl group, for example a methyl group, provided R_3 is correspondingly larger. R_2 and R_3 taken together are preferably alkyl groups containing a total of 15 to 36 carbon atoms. For secondary amines sufficient solubility in preferred organic solvents may generally be achieved if R_2 and R_3 are straight chain or branched chain alkyl groups. However for primary amides (R_2 is hydrogen), R_3 is preferably a branched chain alkyl group. When n is 2, and the groups R_2 and R_3 are all alkyl groups, the total number of alkyl carbon atoms preferably does not exceed 70, for example the total number of alkyl carbon atoms is preferably from 20 to 70.

The process of the present invention is especially applicable to the solvent extraction of coper from aqueous solutions obtained by the halide or pseudo halide leaching of sulphur-containing copper ores, for example from solutions obtained by the leaching of ores such as chalcopyrite with aqueous ferric chloride or cupric chloride solutions.

The leaching of ores such as complex sulphide ores, for example chalcopyrite with for example aqueous ferric chloride solution containing hydrochloric acid gives rise to leach solutions containing cuprous and cupric ions, ferrous and ferric ions and excess chloride anion. The ratio of cuprous to cupric ion depends on the leach conditions selected. The sulphur content of the ore may be precipitated as elemental sulphur. Whilst the scope of the present invention is not to be taken as being limited to the treatment of any particular halide-containing aqueous solution, typical solutions obtained by the leaching of chalcopyrite with acidified ferric chloride may contain between 10 and 60 grams per liter of copper, between 50 and 150 grams per litre of iron, may typically be between 0.1M and 1M in hydrochloric acid and may be between about 2M and 8M in total chloride ion. Certain leach systems may give total chloride ion contents as high as 10M or 12M. All leach solutions encountered in practice will also contain varying quantities of the many other metals present in the ore body. Certain leach solutions may contain high levels of specific metals, for example zinc, in addition to copper.

It will be appreciated that the process of the present invention may be incorporated into a wide variety of different methods for the overall recovery of metals from their ores or from other metal-bearing sources. Details of these methods will vary depending on the metal concerned and the nature and composition of the leach solution. Whilst the process of the present invention is not limited to any single overall method for the recovery of metals, the stringent conditions imposed on the pyridine extractant are best illustrated if the solvent extraction process is seen as a step in an integrated process for the recovery of the metal from the ore. For example an integrated process which is especially suitable for leach solutions containing high levels of cupric ion comprises the following steps:

1. Leaching of the ore with aqueous ferric or cupric chloride solutions, and removing the elemental sulphur produced;

2. Contacting the leach solution from step 1 (in which the ferric ion is at least partially reduced to ferrous ion) with a solution in a water-immiscible solvent of the extractant, whereby the copper is transferred into the organic phase in the form of a chloride-containing complex with the extractant;

3. Separating the organic phase containing the complex of copper with the extractant from the aqueous phase containing the ferric/ferrous chloride;

4. Contacting the organic phase from step 3 with an aqueous strip solution which is water, or which contains a reduced concentration of chloride ion, whereby the chloride-containing complex of copper with the extractant is unstable and copper transfers into the aqueous strip solution;

5. Separating the organic phase containing the stripped extractant from the aqueous strip solution containing the copper chloride; and

6. Electrolysing the strip solution from step 5 to recover copper. The electrolysis step is suitably arranged such that oxidation of ferrous ion with transfer of chloride ion takes place in the anode compartment, such that the solution leaving the cathode compartment is denuded in both copper and chloride ion. Alternatively chlorine gas may be evolved at the anode and optionally used as oxidant to regenerate the leach solution.

In order to preserve the overall stoichiometry of the sequence of reactions, it may be necessary to provide additional oxidation of ferrous to ferric ion, and to remove the ion entering the system continuously from the chalcopyrite ($CuFeS_2$), for example in the form of iron oxide such as goethite.

For a fully integrated process it is highly desirable that the solutions be re-circulated between the various stages. Thus aqueous strip solution used in step 4 is preferably derived from the electrolysis step 6 and is preferably the solution leaving the cathode compartment denuded in both copper and chloride ion. Similarly the organic phase containing the stripped extractant which is separated in step 5 is preferably re-circulated to the extraction stage 2. The ferric chloride solution derived from the electrolysis step 6 may be returned for further leaching of the ore.

Considering first the extraction stage 2 and the strip stage 4, the extraction of for example cupric ion by the extractant may be represented by an equation such as the following:

$$2L_{org} + Cu^{++}{}_{aq} + 2Cl^-{}_{aq} \rightleftharpoons (L_2CuCl_2)_{org}$$
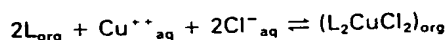
This equation is a grossly oversimplified representation of a very complex process and is not to be taken as in any way limiting the scope of the present invention, but it serves to illustrate the formation of a neutral

organic phase complex of copper and the extractant (L) which is believed to predominate in the process of the present invention. Other equations may be used to represent the extraction and stripping of cuprous ion or of other metals by the extractant.

The above equation assumes that the extractant acts as a monodentate ligand, and whilst this is believed to be generally true, esters and amides of 2-carboxypyridines do at least have the potential of acting as bidentate ligands. Under certain conditions other species, for example oligomeric complexes such as $L_2(CuCl_2)_n$ may be formed. The formation of oligomeric species is generally undesirable since the efficiency of copper extraction is reduced and in addition the oligomeric complexes tend to have a low solubility in organic solvents. We have found that the tendency to the formation of oligomeric species is especially low with esters and amides of 2-carboxypyridines.

The equation also illustrates the reversible nature of the extraction, whereby the complex of copper and the extractant in the organic phase can be stripped on contact with water or with an aqueous solution containing a reduced chloride or a reduced copper content such that copper is transferred to the aqueous phase and the free extractant is at least partially regenerated in the organic phase.

Most efficient stripping will be obtained using water itself as the stripping medium, and the process of the present invention may be combined with a water stripping stage. However, it will be noted that in a fully integrated process, it is preferred that the loaded extractant be stripped with the solution derived from the electrolysis stage and denuded in copper and chloride ion. In an extreme case, the aqueous phase may be entering the electrolysis cell containing about 40 or 50 grams per litre copper and may leave it still containing as much as 30 grams per litre copper or more. The requirement that the extractant will be able to efficiently extract copper from the leach solution, whilst at the same time be stripped by a solution containing relatively high levels of copper is exacting. Preferred extractants for use in the process of the present invention are capable of being stripped by an aqueous solution containing relatively high levels of copper, for example from 20 to 35 grams per litre of copper.

Since the leach solution contains high levels of iron, it is clearly important that the extractant should have good selectivity for copper over iron. The extractants of the present invention have this property. Of particular importance in an integrated system, where the copper is recovered by electrolysis of the pregnant aqueous strip solution, is selectivity for copper over silver and other minor extractable constituents of the ore. The reason for this is that whilst metals such as zinc and cadmium are more electronegative than copper and are not electrodeposited with it, silver is both co-deposited with copper and furthermore adversely affects the physical properties of the copper so that an expensive electrorefining stage is required. Preferred extractants of the present invention have excellent selectivity for copper over silver under appropriate operating conditions.

A yet further property which is of importance for an extractant in the process of the present invention is the absence of significant protonation by the acidic leach liquor. Such protonation may be represented by an equation such as:

$$L_{org} + H^+_{aq} + Cl^-_{aq} \rightleftharpoons (LH^+Cl^-)_{org}$$
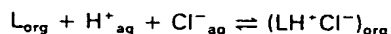
where L is the extractant. Such protonation of the ligand not only carries hydrochloric acid into the organic phase, building up unnecessary chloride concentration on the strip side, but is also believed to be associated with loss of selectivity for copper over silver and other trace components such as antimony and arsenic. Again the preferred extractants of the present invention have excellent resistance to protonation even in contact with relatively acidic leach solutions.

As illustrated by the Examples, the extractants of the present invention provide a range of properties so that the optimum extractant may be selected for a given leach solution. In particular, a "strong" extractant, for example, isooctadecyl nicotinate, is capable of extracting high levels of copper from a leach solution containing relatively low chloride ion content (for example about 3.7M) but tends to undergo undesirable protonation and acid transfer at higher acid/chloride ion concentrations (for example H^+, 0.1M; Cl^-, 9.8M). On the other hand, a "weak" extractant such as a diester of pyridine-2,5-dicarboxylic acid is found to transfer only low levels of acid, even from solutions concentrated in chloride ion and acid (for example 10.7M and 1M respectively). Furthermore the lower inherent ability of the extractant to transfer copper into the organic phase is offset by the improved transfer of copper at these higher chloride ion concentrations.

Bis esters of pyridine-3,5-dicarboxylic acids, for example the bis-nonyl ester, are weak extractants which furthermore show high selectivity for copper over zinc, and provide a potential for recovery of zinc in leach solutions containing high levels of both copper and zinc.

Examples of suitable water-immiscible organic solvents are aliphatic, aromatic and alicyclic hydrocarbons, chlorinated hydrocarbons such as perchloroethylene, trichloroethane and trichloroethylene. Mixtures of solvents may be used. Especially preferred in conventional hydrometallurgical practice are mixed hydrocarbon solvents such as high boiling, high flash point, petroleum fractions (for example kerosene) with varying aromatic content. In general, hydrocarbon solvents having a high aromatic content, for example AROMASOL H which consists of essentially of a mixture of trimethylbenzenes and is commercially available from Imperial Chemical Industries PLC (AROMASOL is a registered trade mark), provide a higher solubility for the extractant and its copper complex, whilst kerosene having a relatively low aromatic content, for example ESCAID 100 which is a petroleum distillate comprising 20% aromatics,

56.6% paraffins and 23.4% naphthenes commercially available from ESSO (ESCAID is a registered trade mark) may in certain cases improve the hydrometallurgical performance of the extractant. Factors influencing the solubility of the extractant and its copper complexes are complicated, but in general extractants having highly branched substituents and/or an isomeric mixture of substituents have comparatively high solubility.

We have found that isonicotinic acid derivatives and their copper complexes, for example (2-hexyldecyl)isonicotinate, have surprisingly high solubility in both high and low aromatic content hydrocarbon solvents.

The concentrations of the extractant in the water-immiscible organic solvent may be chosen to suit the particular leach solution to be treated. Typical values of extractant concentration in the organic phase are between about 0.1 to 2 Molar, and an especially convenient range is from 0.2 to 0.8 Molar in the organic solvent.

The extraction stage and the strip stage of the solvent extraction process may conveniently take place at ambient temperature. However it is possible to improve net copper transfer from the leach solution to the strip solution if the extraction stage is operated at ambient temperature, whilst the strip stage is operated at elevated temperature, for example up to 50°C. We have also found that the undesirable formation and build-up of oligomeric complexes of the extractant and copper may be alleviated if the strip stage is operated at elevated temperatures, for example up to 50°C.

The invention is illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

Example 1

(2-(n)Hexyldecyl)nicotinate was prepared as follows:—

A stirred mixture of nicotinic acid (61.5 parts), dimethylformamide (0.63 parts) and xylene (174 parts) was heated to 80° below a condenser set for reflux. Thionyl/chloride (65.5 parts) was then added during 1—2 hours, the temperature of the reaction mixture being allowed to rise to 90—95° during the addition. The mixture was then stirred at 90—95° for 3 hours. The condenser was then set for distillation and the temperature was raised until excess thionyl chloride had distilled and xylene had begun to distil. The mixture was then allowed to cool to 80—85° and 2-(n)hexyldecanol (112 parts) was added during 30 minutes. The mixture was stirred at 80—85° for 2 hours and was then cooled to room temperature, and extracted with a solution of sodium hydroxide (40 parts) in water (165 parts). The xylene solution was washed alkali free with more water, and the xylene was distilled under reduced pressure leaving (2-hexyldecyl)nicotinate [147 parts] as a brown oil. The purity was estimated at 95% by titration of a sample with N/10 perchloric acid in acetic acid medium. The compound was distilled, b.p. 176—184° at 0.4 mm pressure, yielding 109 parts of straw-coloured liquid which was 98—99% pure.

The ability of (2-(n)hexyldecyl)nicotinate to extract copper from aqueous solution containing chloride ion was investigated.

An aqueous solution (A) was made up which was 0.1M in cupric chloride (6.35 gpl copper), and 0.1M in hydrochloric acid, and which contained in addition 250 g/litre of calcium chloride dihydrate. This solution was then agitated for 15 minutes with an equal volume of a solution (B) which was a 0.2M solution of (2-hexyldecyl)nicotinate in AROMASOL H. The layers were allowed to separate and settle, and were separately analysed for copper content. The percentage of the copper initially present in A which had passed into B, was 44.5%. The resultant loaded organic solution B was then stripped with an aqueous solution (C) which was 0.472M in cupric chloride, i.e. one which contained 30 gpl of copper. It was found that copper passed from the organic to the aqueous solution. The percentage of the copper originally present in A which had been transferred to solution C was 25.5%. The transfer of hydrochloric acid from solution A to solution B was negligible.

Extraction of copper by the same extractant from a more strongly acidic solution was also examined. The same solutions and procedure as before were used, except that solution A was 1.0M rather then 0.1M in hydrochloric acid. The percentage of copper extracted into the organic solution (B) and the percentage which finally passed into the aqueous solution of cupric chloride (C) were 47.8% and 30.6% respectively. The amount of hydrochloric acid which passed from solution A to solution B under these extremely acidic conditions was measured. Expressed as a percentage of that which would be transferred if every molecule of the ligand combined with one molecule of hydrochloric acid, the acid transfer was only 1.9%.

The above results are summarised in Table 1.

Example 2

Tridecyl nicotinate was prepared using the method of Example 1 from commercial tridecanol (an isomeric mixture) and nicotinic acid. The product had a boiling point of 136 to 140°C under 0.05 mm pressure and an estimated purity of 100% based on a molecular weight of 305.5.

The ester was evaluated as an extractant for copper from aqueous solution containing chloride ion using the method of Example 1.

The results are presented in Table 1.

Example 3

N,N-di-(n)-octylnicotinamide was prepared using the method of Example 1 from acid and di(n)-octylamine. The product had a boiling point of 180 to 183°C at 0.15 mm pressure and an estimated purity of 95.5%.

The amide was evaluated as an extractant for copper from aqueous solution containing chloride ion using the method of Example 1.

The results are presented in Table 1.

It will be noted that this compound is a stronger extractant than those shown in the previous Examples, and would be more suitably employed for the extraction and subsequent recovery of copper from an aqueous solution of lower concentration of chloride ion. It would also be preferable to strip the extractant with a strip solution which was lower in copper and/or in chloride ion than solution C.

Example 4

(2-(n)-hexyldecyl)isonicotinate was prepared using the method of Example 1 from isonicotinic acid and 2-hexyldecanol. The product had a boiling point of 180 to 190°C at 0.75 mm pressure and an estimated purity of 97.5%

The ester was evaluated as an extractant for copper from aqueous solution containing chloride ion using the method of Example 1.

The results are presented in Table 1.

TABLE 1

Extractant	Transfer of copper (%) from 0.1M HCl		Transfer of copper (%) from 1.0M HCl		Acid co-extracted (%) from 1.0M HCl to B
	to B	to C	to B	to C	
Example 1	44.5	25.5	47.8	30.6	1.9
Example 2	44.6	26.2	47.6	29.8	3.3
Example 3	72.2	15.2	68.2	11.2	18.8
Example 4	51.0	23.8	57.0	31.4	3.0

* For all Examples the acid co-extracted from 0.1M HCl to B was negligible.

Example 5

A solvent extraction circuit was assembled consisting of small scale mixer settler units. The circuit comprised 3 stages of extraction and 2 stages of stripping and pumping was arranged such that over both the extraction and stripping parts of the circuit the organic and aqueous solutions flowed counter current wise.

The aqueous feed solution had the following composition of metals:

Copper (Cu^{2+})	16.0 g per litre
Iron (Fe^{2+})	40.4 g per litre
Silver (Ag$^+$)	18.9 mg per litre

In addition, the solution contained 150 g per litre of calcium chloride added as the dihydrate $CaCl_2.2H_2O$ and contained 3.6 g per litre of hydrochloric acid giving a total chloride ion concentration of 4.23 moles per litre.

The strip solution consisted of an aqueous solution containing 28.9 gpl copper as cupric chloride with no added acid.

The solvent phase comprises a 19.2% by weight solution (0.553 moles per litre) of the extractant of Example 1 dissolved in AROMASAL H.

The pumps and agitators in the circuit were started and the flow rates adjusted to give an organic flow of 33.3 ml/min and aqueous flows of 13.3 ml/min (2.5 to 1 organic to aqueous phase ratio).

After the circuit had been running successfully for 4 working days at an average temperature of 15°C, samples taken from the aqueous raffinate; from the extraction circuit; and of the pregnant strip solution were analysed.

The results obtained are summarised in Table 2.

TABLE 2

	Cu²⁺ gpl	Fe²⁺ gpl	Ag⁺ mg/l (ppm)
Aqueous feed	16.0	40.4	18.9
Raffinate	2.49	39.8	18.4
Strip solution	28.9	0.24	0
Pregnant strip solution	44.5	0.8	0.6

Example 6

(2-(n)-Octyldodecyl)nicotinate was prepared from nicotinic acid and 2-(n)octyldodecanol using the general method of Example 1 with the following minor changes. The temperature after thionyl chloride addition was maintained at 80°C for 2 hours, and after the esterification reaction, the solution was diluted with petroleum ether (60—80°), washed with water to remove acidity and the solvents removed by distillation. The product had a boiling range of 190—200°C at 0.05 mm mercury pressure and an estimated purity of 87.9%.

The ability of (2-(n)octyldodecyl)nicotinate to extract copper from aqueous solution containing chloride ion was investigated.

An aqueous solution (A) was made up which was 0.1M in cupric chloride (6.35 g/l copper), 0.1M in hydrochloric acid and contained 250 g/l of calcium chloride dihydrate, providing a total chloride ion concentration of 3.7M. This solution was shaken for 1 minute with an equal volume of a solution (B) which was a 0.2M solution of (2-(n)-octyldodecyl)nicotinante in ESCAID 100. The layers were allowed to separate, the aqueous layer was analysed for copper and the solvent layer for acid transferred with the copper. The percentage of copper initially present in A which had passed into B was 52%. There was no detectable transfer of hydrochloric acid into B.

These results are summarised in Table 3.

Example 7

Iso-hexadecyl nicotinate was prepared from nicotinic acid and a commercial material, iso-hexadecyl alcohol, obtained from Farbwerke Hoechst AG. The general method of Example 1 was used except that the temperature after thionyl chloride addition was maintained at 80°C for 2 hours, and after the esterification reaction the solution was cooled and washed with 0.5M sodium hydroxide, 0.5M hydrochloric acid and water. The solution was treated with activated carbon (2.5% on the expected weight of product) at 50°C for 1 hour, filtered and the solvent removed under reduced pressure. The light brown oil had an estimated purity of 93.4% and was distilled (boiling range 141—146°C at 0.03 mm mercury pressure) to provide a product of 99.8% estimated purity.

The ester was evaluated as an extractant for copper from aqueous solution containing chloride ion using the method of Example 6.

To evaluate the efficiency of the extractant for use with leach solutions containing higher levels of total chloride ion, the general test method of Example 6 was repeated using a solution (A) which contained cupric chloride (0.1M), hydrochloric acid (0.1M) and 700 g/l calcium chloride dihydrate, giving a total chloride ion concentration of 9.8M.

The results are displayed in Table 3, and indicate that the extractant is more suitable for use with leach solutions having relatively low total chloride ion concentrations (3.7M), since relatively high acid transfer levels occur at high total chloride ion concentrations (9.8M).

Example 8

Isooctadecyl nicotinate was prepared using the method of Example 7 from nicotinic acid and a commercial product, isooctadecyl alcohol, obtained from Farbwerke Hoechst AG. The product had an estimated purity 94.5%.

The isoactadecyl alcohol starting material was analysed by capilary Gas Chromatography and gave traces showing four peaks each of which was approximately the same size. The commercial isooctadecyl alcohol is believed mainly to comprise different geometric isomers of 2,2,4,8,10,10-hexamethyl-5-methylol-undecane.

The ester was evaluated as an extractant for copper from aqueous solution containing chloride ion, using the method of Example 7.

The results are displayed in Table 3, and indicate that the extractant is more suitable for use with leach solutions having relatively low total chloride ion concentrations (3.7M), since relatively high acid transfer levels occur at high total chloride ion concentrations (9.8M).

Example 9

(2-(n)Hexyldecyl)picolinate was prepared from picolinic acid and 2-(n)hexyldecyl alcohol by the general method of Example 1 with the following differences. The temperature after thionyl chloride addition was maintained at 80°C for 2 hours and after the esterification reaction, the solution was diluted with petroleum ether 60—80°, washed with 1M hydrochloric acid and with brine (10% NaCl). The solvents were removed by evaporation and the dark coloured oil distilled (boiling range 176—178°C at 0.07 mm mercury pressure) to give a colourless oil of estimated purity 97.5%.

The ester was evaluated as an extractant for copper from aqueous solutions containing chloride ions by the general method of Examples 6 and 7, except that AROMASOL H was used as solvent. The solvent A contained the higher levels of chloride ion (9.8M) indicated in Example 7 and Table 3. Table 3 shows that the extractant is comparatively well suited for operation using leach solutions containing higher levels of total chloride ion since only 9% transfer of hydrochloric acid took place at a total chloride ion concentration of 9.8M.

Example 10

Isooctadecyl picolinate was prepared using the method of Example 7 from picolinic acid and iso-octadecyl alcohol, the commercial material obtained from Farbwerke Hoechst AG and described in Example 8. The light brown, oily product of the reaction had an estimated purity of 93.5%.

The ester was evaluated as an extractant for copper from aqueous solutions containing chloride ion using the method of Example 7, except that AROMASOL H was used as solvent.

The results are displayed in Table 3, and show that whilst a relatively low extraction of copper takes place from 3.7M total chloride ion solution, good extraction of copper with relatively low acid transfer takes place from 9.8M total chloride ion solution.

Example 11

This bis isodecyl ester of pyridine-3,5-dicarboxylic acid was prepared by the method of Example 1 from pyridine-3,5-dicarboxylic acid and commercial isodecanol (obtained from ICI Petrochemicals Division) using modified amounts of reactants as required by the stoichiometry. Toluene was used as reaction solvent in place of xylene and the temperature was maintained at 80—82°C for 4 hours after the thionyl chloride addition. Following esterification reaction, the solution was cooled, washed with dilute sodium hydroxide solution, 1M hydrochloric acid, 0.5M hydrochloric acid and water. The solution was treated with activated carbon (8% on the expected weight of product), the solvent evaporated at reduced pressure and the residue distilled (boiling range 200—210°C at 0.08 mm mercury pressure) to give a product having estimated purity of 97.5%.

This bis-ester was evaluated as an extractant for copper from aqueous solutions containing chloride ion by the method of Examples 6 and 7.

To evaluate the efficiency of the extractant for use with leach solutions containing both high levels of total chloride ion and high acid levels, the general test method of Examples 6 and 7 was repeated using a solution A which contained cupric chloride (0.1M), hydrochloric acid (1.0M) and calcium chloride dihydrate (700 g/l), giving a total chloride ion concentration of 10.7M.

The results are displayed in Table 3, and show that whilst a relatively low extraction of copper takes place from 3.7M total chloride ion solution, excellent extraction of copper takes place with no acid transfer from solutions containing a total chloride ion concentration of 9.8M, and low acid transfer levels are achieved even when the total chloride ion concentration is 10.7M.

Example 12

The bis nonyl ester of pyridine-2,4-dicarboxylic acid was prepared using the method of Example 1 from pyridine-2,4-dicarboxylic acid and commercial nonanol (obtained from ICI Petrochemicals Division and containing predominantly 3,5,5-trimethylhexanol), with modified amounts of reactants as required by the stoichiometry. After the thionyl chloride addition, the temperature was maintained at 84—85°C for 2 hours whilst after the esterification reaction the product was isolated as described in Example 7. The boiling range of the product was 200—210°C at 0.2 mm mercury pressure and the estimated purity was 100%.

The bis-ester was evaluated as an extractant for copper from aqueous solutions containing chloride by the method of Examples 6 and 11, except that AROMASOL H was used as solvent.

The results are shown in Table 3.

Example 13

The bis-isodecyl ester of pyridine 2,5-dicarboxylic acid was prepared using the method of Example 1 from pyridine-2,5-dicarboxylic acid and commercial isodecanol, obtained from ICI Petrochemicals Division, with modified amounts of reactants as required by the stoichiometry. Toluene was used as solvent for the reaction, in place of xylene, and after the thionyl chloride addition the temperature was maintained at 77—83°C for 1½ hours. After the esterification reaction the product was isolated as described in Example 7, and had a boiling range of 219—221°C at 0.08 mm mercury pressure, and estimated purity of 95.5%.

The bis-ester was evaluated as an extractant for copper from solutions containing chloride by the method of Examples 7 and 11.

The results are displayed in Table 3.

Example 14

N,N-Di-(n)-octyl picolinamide was prepared using the method of Example 1 from picolinic acid and di-(n)-octylamine. After the addition of thionyl chloride, the temperature was maintained at 79—80°C for 5 hours and then raised to distil excess thionyl chloride and a little xylene. The acid chloride suspension was cooled to 48°C and the molten amine was added at 48—74°C over 10 minutes. The reaction was contained at 90°C for 4 hours and the dark brown solution was cooled and washed with water to remove acidity. The solution was treated with activated carbon (10% on the expected weight of product), filtered, the solvent evaporated and the dark brown oil distilled. The product had a boiling range of 175—180°C at 0.15 mm mercury pressure and was dark coloured. It was purified by dissolving in toluene, treating with activated carbon (10% on expected weight of product) and extracting with 2M sodium hydroxide and water. The toluene was removed by evaporation under reduced pressure to give a mid-brown coloured oil of estimated purity 91%.

The amide was evaluated as an extractant for copper from solutions containing chloride ion as in Examples 6 and 7, except that AROMASOL H was used as solvent.

The results are displayed in Table 3.

TABLE 3

Transfer of copper (%) and hydrochloric acid (%) from aqueous solution

Extractant (Example No.)	SOLUTION COMPOSITION					
	HCl 0.1M		HCl 0.1M		HCl 1.0M	
	Calcium chloride 250 g/l Total chloride 3.7M		Calcium chloride 700 g/l Total chloride 9.8M		Calcium chloride 700 g/l Total chloride 10.7M	
	Cu	H	Cu	H	Cu	H
6	52	0				
7	54	0	77	25		
8	49	0	74	25		
9*			73	9		
10*	20	0	68	7		
11	22	0	80	0	79	6
12*			52	0	51	4
13			17	0	29	8
14*			66	21		
25*			23	3		
26*	66	12	89	22		

ESCAID 100 was used as solvent except for those Examples marked * where the solvent was AROMASOL H.

Example 15

The solvent extraction circuit described in Example 5 was used ot evaluate the extractant of Example 1. The feed was:

Copper (Cu^{2+})	25 g/l
Iron (Fe^{2+})	75 g/l
Silver (Ag^{+})	0.028 g/l
Lead (Pb^{2+})	1.5 g/l
Arsenic (As^{3+})	0.2 g/l
Antimony (Sb^{3+})	0.10 g/l
Mercury (Hg^{+})	0.005 g/l

With the exception of silver, which was added as silver nitrate to facilitate dissolution, the metals were in the form of their chlorides. In addition, the solution contained 1.8 g/l of hydrogen chloride, giving a total chloride ion concentration of 3.5 moles per litre.

The strip solution consisted of an aqueous solution containing 29 g/l copper as cupric chloride, adjusted to pH 1.0 with hydrochloric acid.

The solvent phase comprised 175 g/l (0.5M) of the extractant of Example 1 dissolved in AROMASOL H.

The operating conditions were as described in Example 5, except that the aqueous feed to the first strip mixer-settler was heated, and the stripped organic phase returned to the extraction mixer-settlers was cooled. As a result, the first strip stage operated at an average temperature of 45°C, whilst the second strip stage operated at an average temperature of 34°C. The extraction stages operated at 28°C.

The circuit was operated for 53.5 hours with steady transfer of copper from the aqueous feed solution to the strip solution throughout the period of operation as indicated by analysis of solutions passing through the circuit at the times listed below:

Time (hours)	Cu^{2+} g/l		
	Raffinates	Stripped Organic	Pregnant Strip Soln.
12	8	12	45
40	10	9	49
45	9	10	43
53.5	8	10	41

During the period of operation, analysis for the minor metals present in the feed gave the following results (g/l):

	Ag^{+}	Pb^{2+}	As^{3+}	Sb^{3+}	Hg^{+}
Strip solution	0.001	0.015	0.004	0.010	0.0002
Pregnant strip solution	0.001	0.030	0.008	0.012	0.0002

By way of comparison, the circuit was operated under identical conditions, except that no heating of the strip circuit was used, and all mixer-settlers operated at ambient temperature (22°C). No precipitate was observed but a gradual build-up of an oligomeric copper complex species was inferred from copper loadings on the extractant greater than that expected from the species L_2CuCl_2, where L represents the extractant. The circuit was operated for 30 hours, and during this period, the concentration of copper in both the raffinate and the stripped organic phase steadily increased as indicated below:

Time (hours)	Raffinate (Cu^{2+} g/l)	Stripped organic (Cu^{2+} g/l)
10	10.5	11.4
20	13.4	13.3
30	15.2	15.0

Example 16

The nicotinic acid ester of 2,2,4,8,10,10-hexamethyl-5-methylolundecane (the latter being derivable from the self condensation of two molecules of

$$HOCH_2C_2HCH—CH_2C(CH_3)_3$$
$$|$$
$$CH_3$$

via the Guerbet reaction) was prepared using the method of Example 1. The product had a boiling point of 145 to 150°C at 0.1 mm pressure and an estimated purity of 90.8%.

The ester was evaluated as an extractant for copper from aqueous solution containing chloride ion using the method of Example 1.

The results are as follows:

	%
Transfer of copper from 0.1M HCl to B	42.5
Transfer of copper from 0.1M HCl to C	23.6
Transfer of copper from 1.0M HCl to B	48.0
Transfer of copper from 1.0M HCl to C	30.2
Acid co-extracted from 1.0M HCl to B	2.6

The acid co-extracted from 0.1M HCl to B was negligible.

Examples 17 to 23

The effect of different ester groups on the solubility of a ligand-copper^{II} chloride complex in concentrated solution in a non-polar solvent was examined as follows: Pyridine 3,5-dicarboxylic acid bis esters were prepared by esterifying pyridine, 3,5-dicarboxylic acid with a series of different alcohols according to the procedure of Example 11 (see Table 4). Each ester in turn was made up as a 0.5M solution in ESCAID 100 and loaded with copper^{II} chloride (to approximately 75% of the theoretical amount according to the stoichiometry of L_2CuCl_2 where L is the bis ester) by shaking with twice its volume of an aqueous solution which was 0.1M in HCl, 0.4M in $CuCl_2$ and which in addition contained 250 g/l of calcium chloride dihydrate. Any separation of the metal ligand complex from the organic solution was noted (Test 1). If no separation occurred, the organic solution was loaded to approximately 100% of theoretical by shaking with a second aqueous solution which differed from the first only in containing 500 g/l of calcium chloride dihydrate. Again any separation of complex from the organic solution was noted (Test 2). Results are listed below in Table 4.

TABLE 4

Example	Alcohol used	Test 1	Test 2
18	Mixed isomer iso-octanol	Immediate precipitation occurred	—
19	2-ethylhexanol	"	—
20	Commercial nonanol (3,5,5-trimethylhexanol)	"	—
21	Diisobutyl carbinol	No precipitation	Precipitation occurred after 2 weeks
22	Mixed isomer isononanol*	"	No precipitation after 2 weeks
23	Mixed isomer isodecanol	"	"
24	Mixed isomer tridecanol	Some precipitation occurred but only after 2 weeks	—

* The mixed isomer isononanol was obtained by hydroformylation of a mixed octene stream.

The results indicate that the bis esters of Examples 18, 19, 20, 21 and 24 would require to be used in more dilute solution or in a more polar solvent than ESCAID 100, for example a solvent having a higher aromatic content, but taht the bis esters of Examples 22 and 23 and their copper complexes have excellent solubility even in concentrated solution in a very weakly polar solvent of low aromatic content.

Example 24

N,N,N',N'-tetraisoamyl pyridine-2,5-dicarboxamide was prepared using the method of Example 1 from pyridine-2,5-dicarboxylic acid and diisoamylamine. The crude product in toluene solution was washed several times with 0.5M aqueous sodium hydroxide and then with 0.5M aqueous hydrochloric acid and water. The solution was then treated with charcoal and filtered. The solvent was distilled under reduced pressure, but the product, a brown oil, was not itself distilled. It was made up as a 0.2M solution in AROMASOL H and tested for extraction of copper in the presence of chloride ion using the method of Examples 6 and 7 except that AROMASOL H was used as a solvent. The results are given in Table 3. The results indicate that this is a very weak extractant suitable for recovering copper from aqueous solution of high chloride ion concentrations.
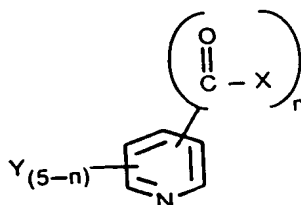
Example 25

3-hexylundecylamine was prepared from 2-hexyldecanol as follows. The alcohol was heated to 96—107° and stirred whilst a stream of hydrogen bromide gas was bubbled through it for 4 hours. The organic layer was separated, and washed first with 96% sulphuric acid and then with water, aqueous ammonia until neutral, and water, and then distilled yielding 1-bromo-2-hexyldecane (b.p. 140° at 1 mm pressure). The bromo compound was converted to 1-cyano-2-hexyldecane by stirring it at the reflux temperature with excess of a 44% aqueous solution of sodium cyanide, in the presence of methyl trioctyl ammonium chloride as a phase transfer catalyst, following C. M. Starks (Journal of the American Chemical Society, 93, page 195, 1971). After washing with dilute aqueous sodium hydroxide solution and water, the cyano compound (141 grams) was dissolved in ethanol (130 ml) and poured into an autoclave. Liquid ammonia (150 g) was added and the autoclave was pressurised to 50 atmospheres with hydrogen, sealed, and heated to 170° for 24 hours. The autoclave was cooled, and most of the ammonia allowed to evaporate. The solution was filtered and the solvent was distilled under reduced pressure. It was found by gas chromatography that complete conversion to 3-hexylundecylamine had taken place.

N,N'-bis(3-hexylundecyl)pyridine-2,5-decarboxamide was prepared using the method of Example 1 from 3-hexylundecylamine and pyridine 2,5-dicarboxylic acid. The product which was a brown oil was not distilled but was analysed as being 92% of theoretical strength (based on MW 642) by titration of an aliquot in acetic acid with perchloric acid. It was made up as a 0.2M solution in AROMASOL H and tested for extraction of copper in the presence of chloride ion using the method of Examples 6 and 7. The results are given in Table 3. They indicated that this compound is a strong extractant for copper which would be best employed in extracting copper from solutions of relatively low chloride ion concentration and relatively low acidity.
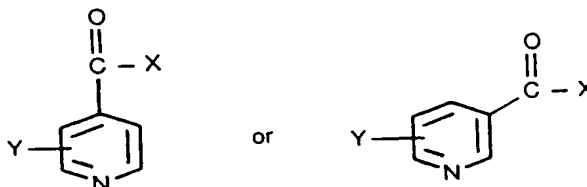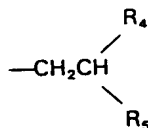
Claims

1. A solvent extraction process for extracting copper values from aqueous solutions of copper salts containing halide or pseudo halide anion which comprises the steps of (1) contacting the aqueous solution containing copper salts with a solution of an extractant in a water-immiscible organic solvent; (2) separating the aqueous solution from the solution of the extractant in the water-immiscible solvent into which copper has been extracted in the form of a complex of the copper and the extractant; and (3) contacting the resultant organic phase with an aqueous strip solution whereby the complex of copper with the extractant is unstable and copper transfers into the aqueous strip solution characterised in that the aqueous solution of copper salts containing halide or pseudo halide anion is contacted with a solution in a water-immiscible organic solvent of an extractant which is a substituted pyridine of formula:

wherein X is the group —OR$_1$ or —NR$_2$R$_3$, R$_1$ being a hydrocarbyl group containing from 5 to 36 carbon atoms and R$_2$ and R$_3$ being hydrogen or a hydrocarbyl group, R$_2$ and R$_3$ together containing from 5 to 36 carbon atoms, and n is 1, 2 or 3; and wherein Y is absent or is one or more of the substituents halogen, alkyl, aryl, alkoxy, aryloxy, aralkyl, cyano, nitro or carboxylic acid.

2. A solvent extraction process for extracting copper values from aqueous solutions of copper salts containing halide or pseudo halide anion which comprise the steps of (1) contacting the aqueous solution containing copper salts with a solution of an extractant in a water-immiscible organic solvent; (2) separating the aqueous solution from the solution of the extractant in the water-immiscible solvent into which copper has been extracted in the form of a complex of the copper and the extractant; and (3) contacting the resultant organic phase with an aqueous strip solution whereby the complex of copper with the extractant is unstable and copper transfers into the aqueous strip solution characterised in that the aqueous solution of copper salts containing halide or pseudo halide anion is contacted with a solution in a water-immiscible organic solvent of an extractant which is a substituted pyridine of formula:

wherein X is the group —OR$_1$ or —NR$_2$R$_3$, R$_1$ being a hydrocarbyl group containing from 5 to 36 carbon atoms and R$_2$ and R$_3$ being hydrogen or a hydrocarbyl group, R$_2$ and R$_3$ together containing from 5 to 20 carbon atoms, and wherein Y is absent or is one ore more of the substituents halogen, alkyl, aryl, alkoxy, aryloxy, aralkyl, cyano, nitro or carboxylic acid.

3. A process according to claim 1 wherein n is 1, X is the group —OR$_1$ and R$_1$ is a branched chain or mixed isomer alkyl group containing from 9 to 24 atoms.

4. A process according to claim 1 wherein n is 1, 2 or 3, X is the group —OR$_1$ and R$_1$ is the group

wherein R$_4$ and R$_5$ are alkyl groups, and R$_4$ contains two fewer carbon atoms than R$_5$.

5. A process according to claim 1 wherein n is 1, Y is absent, X is the group —OR$_1$ and R$_1$ is selected from the group consisting of tridecyl, 2-hexyldecyl, isohexadecyl and 2-oxtyldecyl.

6. A process according to claim 1 wherein n is 2, X is the group —OR$_1$ and the two groups R$_1$ are alkyl groups together containing a total of from 16 to 36 carbon atoms.

7. A process according to claim 6 wherein the two respective groups R$_1$ are the same and contain a mixture of isomers.
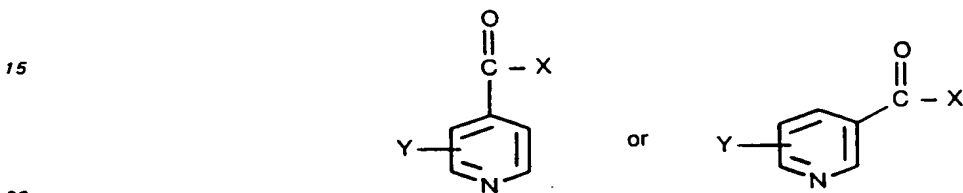
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8. A process according to claim 1 wherein n is 1, X is the group —NR_2R_3 and R_2 is hydrogen or an alkyl group and R_3 is an alkyl group and R_2 and R_3 taken together contain a total of from 15 to 36 carbon atoms, provided that when R_2 is hydrogen, R_3 is a branched chain alkyl group.

9. A process according to claim 1 wherein n is 2, X is the group —NR_2R_3 and the respective groups R_2 and R_3 are alkyl groups and the total number of alkyl carbon atoms is from 20 to 70.

10. A process according to claim 1, wherein n is 2, Y is absent, X is the group —OR_1 and the two respective groups R_1 are the same and are selected from the group consisting of mixed isomer isodecyl, single isomer nonyl, mixed isomer nonyl, 2-ethylhexyl, mixed isomer octyl, di-isobutylcarbinyl and tridecyl.

11. A process according to any of the preceding claims wherein the aqueous strip solution is water or contains a reduced concentration of halide (or pseudo halide) ion.

12. A 3- or 4-substituted pyridine of formula:

wherein X is the group —OR_1 or —NR_2R_3, and wherein when X is the group —OR_1, R_1 is an alkyl group containing from 9 to 24 carbon atoms and having the formula:
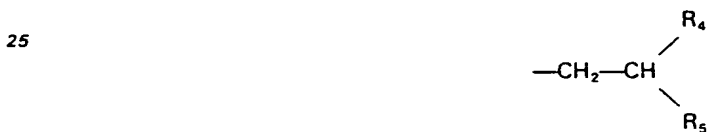
wherein R_4 and R_5 are alkyl groups, and R_4 contains two fewer carbon atoms than R_5, and wherein when X is the group —NR_2R_3, R_2 is hydrogen or an alkyl group, R_3 is an alkyl group and R_2 and R_3 together contain a total of from 15 to 36 carbon atoms, provided that when R_2 is hydrogen, R_3 is a branched chain alkyl group, and wherein Y is absent or is one or more of the substituents halogen, alkyl, aryl, alkoxy, aryloxy, aralkyl, cyano, nitro or carboxylic acid.

13. A substituted pyridine of formula:

wherein the respective groups R_1 and R_6 are branched chain or mixed isomer alkyl groups together containing a total of from 16 to 36 carbon atoms, and wherein Y is absent or is one or more of the substituents halogen, alkyl, aryl, alkoxy, aryloxy, aralkyl, cyano, nitro or carboxylic acid.

14. A substituted pyridine according to claim 13 wherein Y is absent and the respective group R_1 and R_6 are the same and are selected from the group consisting of mixed isomer isodecyl, single isomer nonyl, mixed isomer nonyl, 2-ethylhexyl, mixed isomer octyl, di-isobutylcarbinyl and tridecyl.

15. A substituted pyridine of formula:—

wherein X is the group —OR_1, n is 2 and the two respective groups R_1 are the same and are selected from the group consisting of mixed isomer isodecyl, mixed isomer nonyl, and mixed isomer tridecyl.

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Patentansprüche

1. Lösungsmittelextraktionsverfahren zum Extrahieren von Kupferwerten us wäßrigen Lösungen von Kupfersalzen, die Halogenid- oder Pseudohalogenidanion enthalten, mit den folgenden Schritten: (1) Inberührungbringen der wäßrigen Lösung, die Kupfersalze enthalt, mit einer Lösung eines Extraktionsmittels in einem nicht mit Wasser mischbaren organischen Lösungsmittel; (2) Abtrennen der wäßrigen Lösung von der Lösung des Extraktionsmittels in dem nicht mit Wasser mischbaren Lösungsmittel, in die Kupfer in Form eines Komplexes des Kupfers und des Extraktionsmittels extrahiert worden ist; und (3) Inberührungbringen der erhaltenen organischen Phase mit einer wäßrigen Wasch- bzw. Rück-extrahierlösung, wodurch der Komplex des Kupfers mit dem Extraktionsmittel unstabil ist und Kupfer in die wäßrige Waschlösung übertritt, dadurch gekennzeichnet, daß die wäßrige Lösung von Kupfersalzen, die Halogenid- oder Pseudohalogenidanion enthält, mit einer Lösung eines Extraktionsmittles, das ein substituiertes Pyridin der Formel:
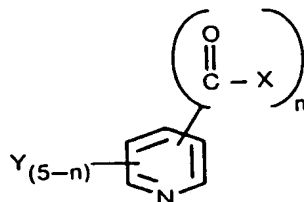
ist, worin X die Gruppe —OR_1 oder —NR_2R_3 ist, wobei R_1 eine Hydrocarbylgruppe ist, die 5 bis 36 Kohlenstoffatome enthält, und R_2 und R_3 Wasserstoff oder eine Hydrocarbylgruppe bedeuten, wobei R_2 und R_3 zusammen 5 bis 36 Kohlenstoffatome enthalten, und n 1, 2 oder 3 ist und worin Y fehlt oder einen oder mehr als einen der Substituenten Halogen, Alkyl, Aryl, Alkoxy, Aryloxy, Aralkyl, Cyano, Nitro oder Carboxyl bedeutet, in einem nicht mit Wasser mischbaren organischen Lösungsmittel in Berührung gebracht wird.

2. Lösungmittelextraktionsverfahren zum Extrahieren von Kupferwerten aus wäßrigen Lösungen von Kupfersalzen, die Halogenid- oder Pseudohalogenidanion enthalten, mit den folgenden Schritten: (1) Inberührungbringen der wäßrigen Lösung, die Kupfersalze enthält, mit einer Lösung eines Extraktionsmittels in einem nicht mit Wasser mischbaren organischen Lösungsmittel; (2) Abtrennen der wäßrigen Lösung von der Lösung des Extraktionsmittels in dem nicht mit Wasser mischbaren Lösungsmittel, in die Kupfer in Form eines Komplexes des Kupfers und des Extraktionsmittels extrahiert worden ist; und (3) Inberührungbringen der erhaltenen organischen Phase mit einer wäßrigen Wasch- bzw. Rückextrahier-lösung, wodurch der Komplex des Kupfers mit dem Extraktionsmittel unstabil ist und Kupfer in die wäßrige Waschlösung übertritt, dadurch gekennzeichnet, daß die wäßrige Lösung von Kupfersalzen, die Halogenid- oder Pseudohalogenidanion enthält, mit einer Lösung eines Extraktionsmittels, das ein substituiertes Pyridin der Formel:
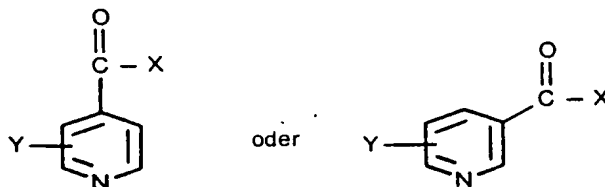
ist, worin X die Gruppe —OR_1 oder —NR_2R_3 ist, wobei R_1 eine Hydrocarbylgruppe ist, die 5 bis 36 Kohlenstoffatome enthält, und R_2 und R_3 Wasserstoff oder eine Hydrocarbylgruppe bedeuten, wobei R_2 und R_3 zusammen 5 bis 20 Kohlenstoffatome enthalten, und worin Y fehlt oder einen oder mehr als einen der Substituenten Halogen, Alkyl, Aryl, Alkoxy, Aryloxy, Aralkyl, Cyano, Nitro oder Carboxyl bedeutet, in einem nicht mit Wasser mischbaren organishen Lösungsmittel in Berührung gebracht wird.

3. Verfahren nach Anspruch 1, bei dem n 1 ist, X die Gruppe —OR_1 ist und R_1 eine verzweigtkettige oder gemischte isomere Alkylgruppe ist, die 9 bis 24 Kohlenstoffatome enthält.

4. Verfahren nach Anspruch 1, bei dem n 1, 2 oder 3 ist, X die Gruppe —OR_1 ist und R_1 die Gruppe
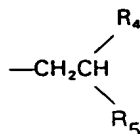
ist, worin R_4 und R_5 Alkylgruppen sind und R_4 zwei Kohlenstoffatome weniger enthält als R_5.

5. Verfahren nach Anspruch 1, bei dem n 1 ist, Y fehlt, X die Gruppe —OR_1 ist und R_1 aus der Gruppe ausgewählt ist, die aus Tridecyl, 2-Hexyldecyl, Isohexadecyl und 2-Octyldecyl besteht.

6. Verfahren nach Anspruch 1, bei dem n 2 ist, X die Gruppe —OR_1 ist und die zwei Gruppen R_1 Alkylgruppen sind, die zusammen insgesamt 16 bis 36 Kohlenstoffatome enthalten.

7. Verfahren nach Anspruch 6, bei dem die zwei einzelnen Gruppen R_1 gleich sind und eine Mischung von Isomeren enthalten.

8. Verfahren nach Anspruch 1, bei dem n 1 ist, X die Gruppe —NR_2R_3 ist und R_2 Wasserstoff oder eine Alkylgruppe ist und R_3 eine Alkylgruppe ist und R_2 und R_3 zusammengenommen insgesamt 15 bis 36 Kohlenstoffatome enthalten, wobei R_3 unter der Bedingung, daß R_2 Wasserstoff bedeutet, eine verzweigtkettige Alkylgruppe ist.

9. Verfahren nach Anspruch 1, bei dem n 2 ist, X die Gruppe —NR_2R_3 ist und die einzelnen Gruppen R_2 und R_3 Alkylgruppen sind und die Gesdamtzahl der Alkyl-Kohlenstoffatome 20 bis 70 beträgt.

10. Verfahren nach Anspruch 1, bei dem n 2 ist, Y fehlt, X die Gruppe —OR_1 ist und die zwei einzelnen Gruppen R_1 gleich sind und aus der Gruppe ausgewählt sind, die aus gemischtem isomerem Isodecyl, einzelnem isomerem Nonyl, gemischtem isomerem Nonyl, 2-Ethylhexyl, gemischtem isomerem Octyl, Di-isobutylcarbinyl und Tridecyl besteht.

11. Verfahren nach einem der vorhergehenden Ansprüche, bei dem die wäßrige Wasch- bzw. Rückextrahierlösung Wasser ist oder eine verminderte Konzentration von Halogenidion (oder Pseudo-halgenidion) enthält.

12. In 3- oder 4-Stellung substituiertes Pyridin der Formel:
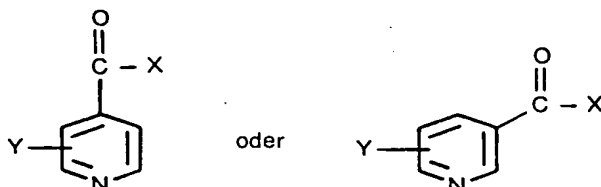
oder

worin X die Gruppe —OR_1 oder —NR_2R_3 ist, wobei in dem Fall, daß X die Gruppe —OR_1 ist, R_1 eine Alkylgruppe ist, die 9 bis 24 Kohlenstoffatome enthält und die Formel:

$$-CH_2CH\begin{array}{c} \nearrow R_4 \\ \searrow R_5 \end{array}$$
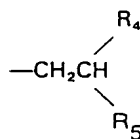
hat, worin R_4 und R_5 Alkylgruppen sind und R_4 zwei Kohlenstoffatome weniger enthält als R_5, und wobei in dem Fall, daß X die Gruppe —NR_2R_3 ist, R_2 Wasserstoff oder eine Alkylgruppe ist, R_3 eine Alkylgruppe ist und R_2 und R_3 zusammen insgesamt 15 bis 36 Kohlenstoffatome enthalten, wobei R_3 unter der Bedingung, daß R_2 Wasserstoff bedeutet, eine verzweigtkettige Alkylgruppe ist, und worin Y fehlt oder einen oder mehr als einen der Substituenten Halogen, Alkyl, Aryl, Alkoxy, Aryloxy, Aralkyl, Cyano, Nitro oder Carboxyl bedeutet.

13. Substituiertes Pyridin der Formel:
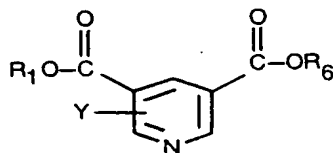
worin die einzelnen Gruppen R_1 und R_6 verweigtkettige oder gemischte isomere Alkylgruppen sind, die zusammen insgesamt 16 bis 36 Kohlenstoffatome enthalten, und worin Y fehlt oder einen oder mehr als einen der Substituenten Halogen, Alkyl, Aryl, Alkoxy, Aryloxy, Aralkyl, Cyano, Nitro oder Carboxyl bedeutet.

14. Substituiertes Pyridin nach Anspruch 13, worin Y fehlt und die einzelnen Gruppen R_1 und R_6 gleich sind und aus der Gruppe ausgewählt sind, die aus gemischtem isomerem Isodecyl, einzelnem isomerem Nonyl, gemischtem isomerem Nonyl, 2-Ethylhexyl, gemischtem isomerem Octyl, Di-isobutylcarbinyl und Tridecyl besteht.

15. Substituiertes Pyridin der Formel:

$$\left(\begin{array}{c} O \\ \| \\ C-X \end{array} \right)_n$$
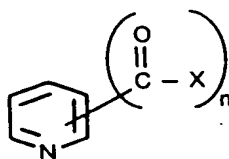
worin X die Gruppe —OR₁ ist, n 2 ist und die zwei einzelnen Gruppen R₁ gleich sind und aus der Gruppe ausgewählt sind, die aus gemischtem isomerem Isodecyl, gemischtem isomerem Nonyl und gemischtem isomerem Tridecyl besteht.
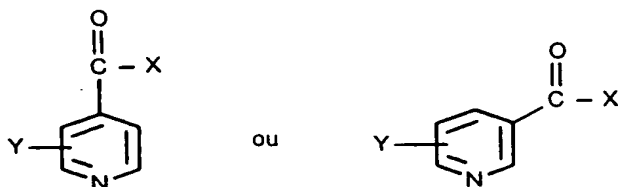
Revendications

1. Procédé d'extraction en solvant pour extraire le cuivre de solutions aqueuses de sels de cuivre contenant un anion halogénure ou pseudohalogénure, qui comprend les stades (1) de mettre la solution aqueuse contenant les sels de cuivre en contact avec une solution d'un agent d'extraction dans un solvant organique non miscible à leau; (2) de séparer la solution aqueuse de la solution de l'agent d'extraction dans le solvant non miscible à l'eau dans laquelle le cuivre a été extrait sous la forme d'un complexe du cuivre et de l'agent d'extraction; et (3) de mettre la phase organique résultante en contact avec une solution aqueuse d'épuisement de façon que le complexe de cuivre avec l'agent d'extraction soit instable et que le cuivre se transfère dans la solution aqueuse d'épuisement, caractérisé en ce que la solution aqueuse de sels de cuivre contenant un anion halogénure ou pseudohalogénure est mise en contact avec une solution, dans un solvant organique non miscible à l'eau, d'un agent d'extraction qui est une pyridine substituée de formule:

$$Y_{(5-n)} - \left(\begin{array}{c} O \\ \| \\ C-X \end{array} \right)_n$$
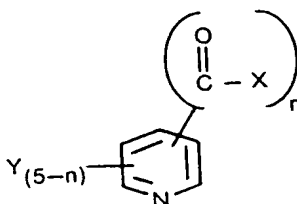
où représente le radical —OR₁ ou —NR₂R₃, R₁ représentant un radical hydrocarbyle comptant 5 à 36 atomes de carbone et R₂ et R₃ représentant un atome d'hydrogène ou un radical hydrocarbyle, R₂ et R₃ comptant ensemble 5 à 36 atomes de carbone et n représente 1, 2 ou 3; et où Y est absent ou représente un ou plusieurs des substituants halogéno, alcoyle, aryle, alcoxy, aryloxy, aralcoyle, cyano, nitro et acide carboxylique.

2. Procédé d'extraction en solvant pour extraire le cuivre de solutions aqueuses de sels de cuivre contenant un anion halogénure ou pseudohalogénure, qui comprend les stades (1) de mettre la solution aqueuse contenant les sels de cuivre en contact avec une solution d'un agent d'extraction dans un solvant organique non miscible à l'eau; (2) de séparer la solution aqueuse de la solution de l'agent d'extraction dans le solvant non miscible à l'eau dans laquelle le cuivre a été extrait sous la forme d'un complexe du cuivre et de l'agent d'extraction; et (3) de mettre la phase organique résultante en contact avec une solution aqueuse d'épuisement de façon que le complexe de cuivre avec l'agent d'extraction soit instable et que le cuivre se transfère dans la solution aqueise d'épuisement, caractérisé en ce que la solution aqueuse de sels de cuivre contenant un anion halogénure ou pseudohalogénure est mist en contact avec une solution, dans un solvant organique non miscible à l'eau, d'une agent d'extraction qui est une pyridine substituée de formule:

$$Y - \begin{array}{c} O \\ \| \\ C-X \end{array} \qquad ou \qquad Y - \begin{array}{c} O \\ \| \\ C-X \end{array}$$

où X représente le radical —OR₁ ou —NR₂R₃, R₁ représentant un radical hydrocarbyle comptant 5 à 36 atomes de carbone et R₂ et R₃ représentant un atome d'hydrogène ou un radical hydrocarbyle. R₂ et R₃ comptant ensemble 5 à 20 atomes de carbone et où Y est absent ou représente un ou plusieurs des substituants halogéno, alcoyle, aryle, alxoxy, aryloxy, aralcoyle, cyano, nitro et acide carboxylique.

3. Procédé d'extraction suivant la revendication 1, dans lequel n représente 1, X représente le radical —OR$_1$ et R$_1$ représente un radical alcoyle en chaîne ramifiée ou isomère mixte comptant 9 à 24 atomes de carbone.

4. Procédé suivant la revendication 1, dans lequel n représente 1, 2 ou 3, X représente le radical —OR$_1$ et R$_1$ représente le radical
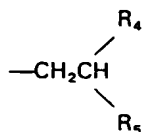
$$-CH_2CH \begin{array}{c} R_4 \\ \diagdown \\ R_5 \end{array}$$

où R$_4$ et R$_5$ représentent des radicaux alcoyle et R$_4$ compte deux atomes de carbone de moins que R$_5$.

5. Procédé suivant la revendication 1, dans lequel n représente 1, Y est absent, X représente le radical —OR$_1$ et R$_1$ est choisi dans la classe formée par les radicaux tridécyle, 2-hexyldécyle, isohexadécyle et 2-octyldécyle.

6. Procédé suivant la revendication 1, dans lequel n représente 2, X représente le radical —OR$_1$ et les deux radicaux R$_1$ sont des radicaux alcoyle comptant ensemble au total 16 à 36 atomes de carbone.

7. Procédé suivant la revendication 6, dans lequel les deux radicaux R$_1$ respectifs sont identiques et contiennent un mélange d'isomères.
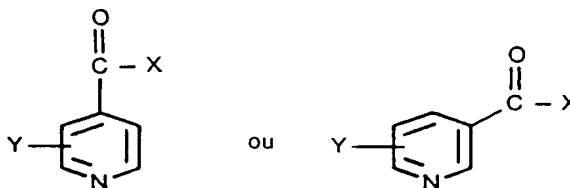
8. Procédé suivant la revendication 1, dans lequel n représente 1, X représente le radical —NR$_2$R$_3$ et R$_2$ représente un atome d'hydrogène ou un radical alcoyle et R$_3$ représente un radical alcoyle et R$_2$ et R$_3$ pris ensemble comptent au total 15 à 36 atomes de carbone, avec la restriction que lorsque R$_2$ représente un atome d'hydrogène, R$_3$ représente un radical alcoyle en chaîne ramifiée.

9. Procédé suivant la revendication 1, dans lequel n représente 2, X représente le radical —NR$_2$R$_3$ et les radicaux R$_2$ et R$_3$ respectifs sont des radicaux alcoyle et le nombre total des atomes de carbon alcoyliques est de 20 à 70.

10. Procédé suivant la revendication 1, dans lequel n représente 2, Y est absent, X représente le radical —OR$_1$ et les deux radicaux R$_1$ respectifs sont identiques et sont choisis dans la classe formée par les radicaux isodécyle isomère mixte, nonyle isomère unique, nonyle isomère mixte, 2-éthylhexyle, octyle isomère mixte, diisobutylcarbinyle et tridécyle.

11. Procédé suivant l'une quelconque des revendications précédentes, dans lequel la solution aqueuse d'épuisement est l'eau ou contient une concentration réduite en ion halogénure (ou psuedohalogénure).

12. Pyridine 3- ou 4-substituée de formule:

ou X représente le radical —OR$_1$ ou —NR$_2$R$_3$ et où, lorsque X représente le radical —OR$_1$, R$_1$ représente un radical alcoyle comptant 9 à 24 atomes de carbone et répondant à la formule:
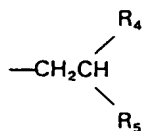
$$-CH_2CH \begin{array}{c} R_4 \\ \diagdown \\ R_5 \end{array}$$

où R$_4$ et R$_5$ représentent des radicaux alcoyle et R$_4$ compte deux atomes de carbone de moins que R$_5$ et où lorsque X représente le radical —NR$_2$R$_3$, R$_2$ représente un atome d'hydrogène ou un radical alcoyle, R$_3$ représente un radical alcoyle et R$_2$ et R$_3$ comptent ensemble au total 15 à 36 atomes de carbone, avec la restriction que lorsque R$_2$ représente un atome d'hydrogène, R$_3$ représente un radical alcoyle en chaîne ramifiée, et où Y est absent ou représente un ou plusieurs des substituants halogéno, alcoyle, aryle, alcoxy, aryloxy, aralcoyle, cyano, nitro et acide carboxylique.

13. Pyridine substitué de formule
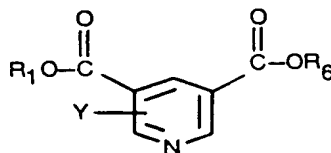
où les radicaux R_1 et R_6 respectifs sont des radicaux alcoyle en chaîne ramifiée ou isomère mixte comptant ensemble au total 16 à 36 atomes de carbone et où Y est absent ou représente un ou plusieurs des substituants halogèno, alcoyle, aryle, alcoxy, aryloxy, aralcoyle, cyano, nitro et acide carboxylique.

14. Pyridine substituée suivant la revendication 13, dans laquelle Y est absent et les radicaux R_1 et R_6 respectifs sont identiques et sont choisis dans la classe formée par les radicaux isodécyle isomère mixte, nonyle isomère unique, nonyle isomère mixte, 2-éthylhexyle, octyle isomère mixtre, diisobutylcarbinyle et tridécyle.

15. Pyridine substituée de formule:
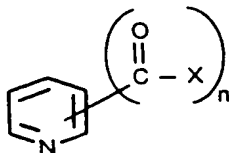
où X représente le radical —OR_1, n représente 2 et les deux radicaux R_1 respectifs sont identiques et sont choisis dans la classe formée par les radicaux isodécyle isomère mixte, nonyle isomère mixtre et tridécyle isomère mixte.